

Article

Clarification of Copper Sulfide Precipitates by Polymeric Microfiltration Membranes

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Abstract

The recovery of copper from metallurgical effluents is critical for advancing sustainable mining and circular economy practices. This study evaluated a hybrid process combining copper sulfide precipitation with clarification using polymeric polyvinylidene fluoride (PVDF) microfiltration membranes. Laboratory-scale experiments were performed under controlled cyanide conditions (100 mg/L free CN[−], 1800 mg/L Cu²⁺), focusing on permeate flux behavior, fouling mechanisms, and cleaning strategies. Optimal performance was achieved at moderate transmembrane pressures (<2.0 bar) and higher flow rates, which provided a balance between productivity and fouling control. Flux decline was attributed to a combination of pore blocking and cake layer formation, confirming the multifactorial nature of fouling dynamics. Cleaning tests revealed that oxidizing solutions (HCl + H₂O₂) restored up to 96% of the initial permeability, while combined treatments with NaCN achieved complete recovery (>100%), albeit with potential risks of membrane aging under prolonged exposure. A techno-economic assessment comparing polymeric and ceramic membranes revealed similar capital and operational costs, with polymeric membranes offering slight reductions in CAPEX (10%) and OPEX (2.3%). Overall, the findings demonstrate the technical feasibility and economic competitiveness of polymeric membranes for copper sulfide clarification, while emphasizing the need to improve long-term chemical resistance to ensure reliable industrial-scale implementation.



Academic Editor: Grzegorz Bartosz

Received: 2 September 2025

Revised: 27 September 2025

Accepted: 11 October 2025

Published: 15 October 2025

Citation: Quilaqueo, M.; Barraza, N.; Barros, L.; Pérez, K.; Ruby-Figueroa, R.; Troncoso, E.; Estay, H. Clarification of Copper Sulfide Precipitates by Polymeric Microfiltration Membranes. *Processes* **2025**, *13*, 3292. <https://doi.org/10.3390/pr13103292>

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Keywords: copper recovery; sulfide precipitation; microfiltration membranes; polymeric membranes; membrane performance; fouling; chemical cleaning; techno-economic assessment

1. Introduction

In the mining and metallurgical sectors, acid mine drainage (AMD) and effluents generated by hydrometallurgical processes are significant sources of metal contamination [1,2]. These waste streams are typically characterized by complex compositions and variable physicochemical properties, influenced by the nature of the raw materials processed and the diverse discharges originating from different stages of mineral processing [2]. Effluents often display low alkalinity, elevated salinity, and high concentrations of metals such as Cu,

Fe, Mn, Zn, Ni, As, and Pb, among others, posing considerable challenges for treatment using conventional technologies [3–8].

The effective treatment of these effluents, particularly the removal of heavy metals, is crucial for achieving United Nations Sustainable Development Goal 6 (SDG 6), which seeks to ensure universal access to clean water and sanitation by 2030 [9]. Treatment strategies are increasingly conceived not only as environmental mitigation measures but also as opportunities for resource recovery, aligning with the principles of the circular economy and sustainable resource management [1,10], among these critical resources.

Copper stands out as a key material for the global energy transition. Forecasts suggest that copper demand could increase by up to 600% by 2030, driven by its essential role in electrification and renewable energy systems [11]. Although copper is relatively abundant, its geographic concentration and strategic relevance across numerous industries, including electronics, construction, transportation, metallurgy, electroplating, and battery manufacturing, underscore the need for efficient recovery strategies [4,7,9,12–18]. Consequently, growing attention has been directed toward the recovery of copper from industrial effluents, particularly those with economically significant concentrations. For instance, previous research has documented copper levels ranging from 80 to 240 mg/L in certain effluents, highlighting the potential for profitable metal recovery operations [19].

Several traditional techniques, such as coagulation, reverse osmosis, ion exchange, and chemical precipitation, are widely employed for copper removal. However, selecting the most suitable technique requires careful consideration of removal efficiency, operational cost, and process feasibility, especially for complex and highly contaminated effluents [15]. Under this scenario, metal sulfide precipitation has emerged as a highly effective approach for the treatment of effluents with high copper content, especially in acidic as observed by Estay et al. (2021) [10] and saline environments and under large-volume conditions [4,20]. This method selectively separates dissolved metals by converting them into highly insoluble sulfide compounds, using reagents such as H_2S , $NaHS$, Na_2S , or CaS . In the case of copper, sulfide precipitates exhibit extremely low solubility, with K_{sp} values between 49.2 and 35.9, making this process particularly attractive for recovery purposes [21]. One notable industrial application of this technique is the SART process (Sulphidization, Acidification, Recycling, and Thickening), implemented in gold cyanidation plants. This integrated process enables the selective removal and recovery of copper, while simultaneously regenerating cyanide, a critical reagent in gold leaching, which can then be recycled into the process circuit [22].

Despite its advantages, a major limitation of metal sulfide precipitation is the solid–liquid separation stage. The resulting precipitates are often colloidal and difficult to settle using conventional sedimentation equipment [23,24]. Furthermore, studies have demonstrated that particle size distribution and settling behavior vary depending on solution composition and sulfide dosage [21,23,25], directly impacting the efficiency of metal recovery and the quality of the treated effluent [21]. Copper sulfide (CuS) samples generally exhibit particle sizes below 74 μm , with mean sizes for different copper sulfide minerals (including CuS) reported in the range of ~23.92 to 50.55 μm [26,27], even reaching values around 1 μm in a fraction of the particle size distribution [25,28]. To address these limitations, membrane-based separation processes such as microfiltration (MF) and ultrafiltration (UF) have been proposed as promising alternatives. These pressure-driven technologies offer several operational benefits, including high separation efficiency, elimination of settling stages, reduced processing time, minimal sludge generation, and easier system maintenance [21,28]. Microfiltration uses membranes with pore sizes between 0.1 and 10 μm , a range that has proven highly effective for achieving strong contaminant removal in water and wastewater treatment. Moreover, because MF systems are both versatile and scalable,

they can be applied successfully in settings that range from small laboratory experiments to full-scale industrial operations [29]. Several studies have reported the successful clarification of metal sulfide suspensions using membrane filtration. For example, MF TiO₂ ceramic monotubular membranes with 0.14 µm pore size have demonstrated high permeate fluxes (>1.0 L/m²·s) when treating copper-rich streams (200–1800 mg/L) generated through sulfide precipitation [21,28]. More recently, membrane clarification has been integrated into processes such as SuCy[®], a copper and cyanide recovery system for gold mining, which reported capital cost reductions of 26–32%, and a 90% reduction in plant footprint due to membrane module implementation [30]. Nevertheless, membrane fouling remains a serious challenge that can compromise the continuity and scalability of these separation technologies [31,32]. Thus, controlling and mitigating fouling is essential for the reliable application of membrane technologies in effluent treatment [5].

The choice of membrane material is a critical factor influencing both capital (CAPEX) and operational expenditure (OPEX). While ceramic membranes offer excellent chemical and thermal resistance, their high production costs and limited availability restrict widespread industrial adoption [3,6,33]. Polymeric membranes, with average prices ranging from 20 to 200 US\$/m², are substantially less expensive than ceramic membranes, which typically cost between 500 and 3000 US\$/m² [34]. In particular, polymeric membranes, such as those made from polysulfone (PSF), polyvinylidene fluoride (PVDF), and cellulose acetate (CA), present cost-effective and flexible alternatives, compatible with moderate operating conditions and more readily scalable for industrial applications [15,16,33]. Among commonly used membrane materials, polysulfone (PSF) demonstrates broad chemical and pH resistance (1–13) but is prone to fouling due to its hydrophobicity [35]; polyvinylidene fluoride (PVDF) demonstrates strong chemical stability and UV resistance, with durability against acids and alkalis within the pH range of 2–12 [36]; whereas cellulose acetate (CA) is limited by its narrower pH range (3–8), lower thermal stability, and susceptibility to microbial degradation [37].

In this context, this study aimed to evaluate a hybrid process that integrates copper sulfide precipitation with membrane-based clarification using a PVDF polymeric microfiltration membrane. The main objective was to determine the technical and economic feasibility of this approach for copper recovery from synthetic effluents. To achieve this, we focused on identifying the type of membrane fouling, assessing chemical cleaning protocols to restore membrane performance, and evaluating the long-term operational stability of the system. Additionally, a preliminary economic analysis was conducted to compare this alternative with more costly technologies, highlighting the potential of polymeric membranes as an efficient and cost-effective solution for clarifying copper sulfide suspensions.

2. Materials and Methods

2.1. Experimental Set-Up and Procedure Under Batch Concentration Configuration

The experimental work was conducted using a laboratory-scale microfiltration (MF) prototype designed to assess the clarification of copper sulfide suspensions. The setup consisted of a flat sheet circular stainless-steel membrane module (model C-SSC-L-60, diameter: 6 cm, DeltaE s.r.l., Quattromiglia, Italy) connected to a sealed glass reactor with a total volume of 2 L. The reactor was equipped with a cooling jacket and an overhead mechanical agitator (model RW20, IKA, Staufen, Germany) to ensure thermal regulation and uniform suspension mixing. The reactor feed was circulated through the membrane module using a diaphragm pump (model F 1.300TT18RC, KNF, Freiburg-Munzingen, Germany). A Coriolis mass flow meter (model Optimass 3400C, Khrone, Duisburg, Germany) was installed downstream of the pump to measure the feed flow rate. A pressure gauge was placed on the retentate outlet line, upstream of a pressure control valve to monitor and

regulate the transmembrane pressure. The permeate was collected in a sealed container positioned on an electronic balance connected to a computer, allowing real-time acquisition of permeate mass over time.

The membrane module was fitted with a flat-sheet PVDF membrane (Sterlitech, Synder, WA, USA) with a pore size of 0.1 μm , a diameter of 6.0 cm, and an active filtration area of 0.0018 m^2 . The membranes exhibited a hydraulic water permeability ranging from 1.5×10^{-8} to $2.3 \times 10^{-8} \text{ m}^3/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$. These values agree with our previous studies performed in ceramic membranes [21,28]. A schematic representation of the experimental setup is provided in Figure 1.

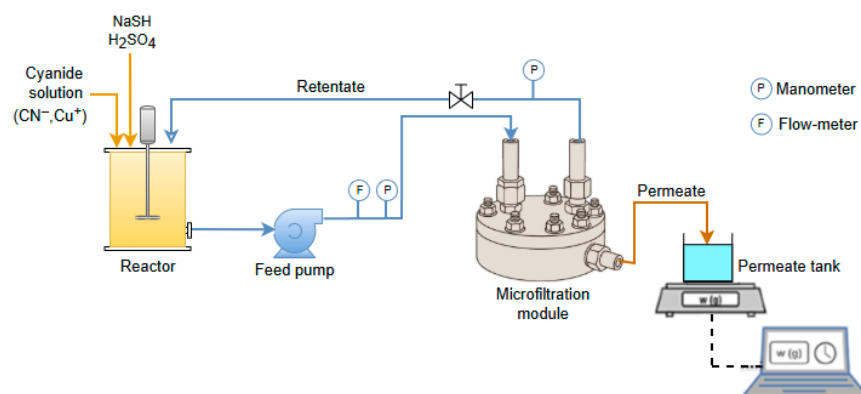
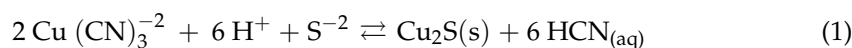


Figure 1. Schematic diagram of the laboratory-scale MF system used for copper sulfide clarification.

All tests were conducted using synthetic cyanide solutions. The free cyanide concentration was set at 100 mg/L, consistent with typical operational conditions employed in gold leaching processes and aligned with criteria adopted in previous studies [28,30,32]. A high copper concentration 1800 mg/L was selected based on prior findings indicating that such levels favor the formation of larger precipitate aggregates, thereby enhancing transmembrane flux during subsequent filtration steps [30]. The total cyanide concentration was determined following the methodology described by Estay et al. (2020) [22], resulting in a total cyanide concentration of 2460 mg/L for the selected copper concentrations of 1800 mg/L.

The precipitation reaction was carried out under previously optimized conditions: a 120% stoichiometric dose of sulfide and a pH of 4.5 [32]. The reaction took place in the stirred glass reactor at 200 rpm for 5 min. This reaction time was defined based on recent kinetic studies of metal sulfide precipitation in cyanide media, which have shown that maximum metal conversion (>98%) is achieved within the first five minutes at the pH and stoichiometric sulfide dosage selected [22]. The precipitation reaction follows the stoichiometry shown below [32]:



The stopping criterion for each test was defined as the point at which the volume of the precipitation reactor reached the minimum level required for pumping (approximately 150 mL). This approach ensured that the total mass of solids processed by the membrane was similar in all experiments, thereby avoiding any influence of varying solids loads on the fouling results.

2.2. Microfiltration Performance

The performance of the microfiltration assays was determined by an experimental matrix comprising five transmembrane pressure (TMP) conditions (1.0, 1.5, 2.0, 3.0, and 3.5 bar) and two feed flow rate conditions (900 and 1100 mL/min). The main performance

indicator was the permeate flux, which was monitored over time and calculated using the following Equation (2):

$$J_w = \frac{\Delta w}{A \cdot \Delta t} \quad (2)$$

where J_w is the permeate flux ($\text{kg}/\text{m}^2 \cdot \text{h}$), Δw is the change in permeate mass (kg) over the time interval Δt (h), and A is the effective membrane area (m^2). Since the permeate density is close to that of water due to its low ionic content, flux expressed in liters ($\text{L}/\text{m}^2 \cdot \text{h}$) is essentially equivalent to that expressed in kilograms ($\text{kg}/\text{m}^2 \cdot \text{h}$).

2.3. Determination of Critical Transmembrane Pressure (CTMP) and Limiting Flux

The CTMP and limiting flux were determined following previously established methodologies for copper sulfide clarification using this membrane system [28,38]. After completing the five-minute precipitation reaction, the resulting suspension was fed into the MF module.

To construct a flux-pressure profile, the TMP was varied between 1.0 and 3.5 bar, while the crossflow rate was adjusted between 900 and 1100 mL/min. These operational conditions enabled the identification of the CTMP and the onset of limiting flux behavior, following criteria established in earlier studies [39,40]. The system was operated in batch concentration mode, with continuous recirculation of the retentate to the stirred reactor. To minimize the volatilization of HCN, the permeate tank was maintained with a 1 M NaOH solution throughout the experiments.

2.4. Membrane Fouling Analysis

Membrane fouling behavior was analyzed using the classical fouling models proposed by Hermia, applied to all pressure and flow rate conditions (900 and 1100 mL/min). These models describe flux decline under constant-pressure filtration and are useful for identifying dominant fouling mechanisms based on fitting parameters. Hermia's general model is expressed as:

$$\frac{d^2t}{dV^2} = K \left(\frac{dt}{dV} \right)^n \quad (3)$$

where t is the filtration time (s), V is the cumulative permeate volume (m^3), K is a fouling rate constant, and n is the model-specific exponent. Each value of n corresponds to a distinct fouling mechanism: $n = 2.0$ relates to complete pore blocking, where each particle that reaches the membrane surface blocks a pore entrance; $n = 1.5$ relates to standard pore blocking, where particles smaller than the pore size enter and reduce pore volume; $n = 1.0$ relates to intermediate blocking, where particles deposit over other adsorbed molecules without fully blocking the pores; and $n = 0$ relates to cake layer formation, where particles form a porous deposit on the membrane surface without penetrating the pores [41].

Given that Hermia's model was originally developed for dead-end filtration, Field and co-workers [39] introduced a modified version suitable for crossflow microfiltration systems, as expressed by:

$$-\frac{dJ}{dt} = K(J - J_{ss})J^{2-n} \quad (4)$$

where J is the instantaneous permeate flux ($\text{L}/\text{m}^2 \cdot \text{s}$), J_{ss} is the steady-state flux ($\text{L}/\text{m}^2 \cdot \text{s}$), K is a fouling constant whose units depend on the value of n , and n is a generalized fouling index that reflects the dominant fouling mechanism and varies accordingly, as previously reported [42].

In crossflow microfiltration, fouling behavior and flow dynamics differ from dead-end filtration due to the presence of tangential flow across the membrane surface. This flow generates shear stress that partially removes or prevents the accumulation of deposited

particles, thereby contributing to the stabilization of the permeate flux and the establishment of a steady-state regime characterized by constant flux [43].

2.5. Feasibility Tests for Membrane Recovery

The membrane cleaning protocol was designed to assess the feasibility of restoring membrane performance and to identify the most effective chemical cleaning agent among the proposed options. The selected reagents were chosen for their ability to solubilize copper sulfide precipitates, facilitating their removal from both the membrane surface and internal pores.

The choice of cleaning agents was informed by previous studies involving ceramic membranes [21] with particular consideration given to the need for oxidative conditions to dissolve Cu_2S , which is poorly soluble under neutral or reducing environments. Three cleaning solutions were evaluated: (i) (9.42 wt%) sodium cyanide, (ii) a mixture of hydrochloric acid (5 wt%) and hydrogen peroxide (46.4 wt%), and (iii) a combined solution containing both systems. It is important to note that the presence of an oxidizing agent is essential for the effective dissolution of copper sulfide. In the case of cyanide alone, oxidation is driven by the dissolved oxygen present in the solution, which promotes the formation of soluble Cu-CN complexes [28]. Following each filtration test, the membrane was removed from the module, and any residual slurry was gently wiped from its surface. The membrane was then immersed in a 1000 mL beaker containing the corresponding cleaning solution. Three contact times (1, 2, and 24 h) were tested for each reagent to determine the impact of exposure time on cleaning effectiveness. At the end of each cleaning cycle, the hydraulic permeability of the membrane was measured to assess the extent of performance recovery. The percentage of membrane recovery was calculated according to the following equation:

$$\text{Recovery (\%)} = \frac{\text{Final permeability (after cleaning)}}{\text{Initial permeability (before potential fouling)}} \times 100 \quad (5)$$

2.6. Statistical Evaluation and Model Validation

The fouling model was evaluated using standard fitting and predictive metrics, namely the coefficient of determination (R^2) and the root mean square percentage error (RMSPE), calculated from the linearized fitting curves. Superior model performance was defined as achieving the highest R^2 , representing the proportion of variance in the data explained by the model, and the lowest RMSPE, reflecting minimal residual error between experimental and predicted values [32]. Model validation also involved testing the normality of residuals, defined as the difference between observed and fitted permeate flux values, using the Shapiro–Wilk (S-W) and Kolmogorov–Smirnov (K-S) tests at a 95% confidence level. Failure to reject the null hypothesis of normality indicated that residuals were unbiased, purely random, and free from systematic patterns unaccounted for by the model, thereby supporting the conclusion that the estimated parameters adequately described the system [32]. All statistical analyses were performed using Statgraphics Centurion 19 (Statgraphics Technologies, The Plains, VA, USA).

2.7. Capital and Operational Cost Comparison

The preliminary economic assessment was based on the estimation reported in the previous study by Estay et al. (2021) [30], which evaluated the SuCy[®] process employing ceramic membranes. In the present work, the only modification introduced was the replacement of the unitary membrane cost, considering polymeric membranes at 60 US\$/m² instead of the 400 US\$/m² reported for ceramic membranes. All other parameters, including

flux values and membrane replacement rates, were kept constant in both cases to isolate and analyze the specific impact of membrane unitary cost on the overall economic performance.

3. Results

The results are presented in five parts, addressing the effect of operating conditions (transmembrane pressure and feed flow rate) on permeate flux, the relationship between TMP and limiting flux, the assessment of fouling mechanisms using Hermia's models modified by Field and co-workers, membrane recovery after cleaning, and the comparative economic analysis of polymeric and ceramic membranes.

3.1. Microfiltration Performance

Permeate flux as a function of time at different TMP values and for the two evaluated operating flow rates is shown in Figure 2. The average flux values for 900 and 1100 mL/min ranged between 0.7 and 2.9 L/m²·s. As expected, higher transmembrane pressures resulted in higher fluxes. Under all tested conditions, flux exhibited a progressive decline over time. For example, at 3.5 bar and 900 mL/min (Figure 2A), the initial flux reached 2.7 L/m²·s but decreased to ~1.6 L/m²·s after 350 s. In contrast, at 1.0 bar it remained relatively stable ranging from 0.8 to 0.9 L/m²·s throughout the experiment. A similar trend was observed at 1100 mL/min (Figure 2B), where initial values were comparable (2.4–2.9 L/m²·s at 3.0–3.5 bar, respectively), but the decline was more pronounced at higher pressures: at 3.5 bar, the flux decreased from 2.9 to 1.3 L/m²·s, and at 3.0 bar from 2.4 to 1.2 L/m²·s. The rapid decline in flux under high-TMP conditions is consistent with previous reports by Estay et al. (2021) [28] and Menzel et al. (2021) [21]. In contrast, tests conducted at 1.0 bar exhibited more stable operation with minimal flux reduction compared to higher TMP values, which can be interpreted as a balance point between productivity and fouling control. Those above confirms that operating in the subcritical region favors flux stability and reduces the risk of irreversible fouling.

Overall, the results demonstrate that membrane performance is strongly dependent on the combination of pressure and flow. Although pressures of 3.0–3.5 bar yield initial fluxes up to three times higher than those observed at 1.0 bar, they rapidly decline and lose their advantage within 600 s of operation. In contrast, intermediate pressures (~2.0 bar) combined with higher flow rates (1100 mL/min) maintained a flux above 1.6 L/m²·s after 400 s, representing a more efficient condition that balances magnitude and stability. Thus, optimal operation appears to lie in moderate pressures coupled with elevated flow rates, which mitigates fouling without significantly compromising productivity.

3.2. CTMP and Limiting Flux

The flux results at different TMP levels are shown in Figure 3. Flux increased almost linearly with pressure in the range of 1.0 to 3.5 bar for both flow rates (900 and 1100 mL/min), confirming that the transmembrane pressure gradient is the main driving force for membrane permeability. At 1.0 bar, the lowest values were recorded (0.8 L/m²·s at 900 mL/min and 0.7 L/m²·s at 1100 mL/min). In contrast at 2.0 bar the flux nearly doubled, reaching 1.7 L/m²·s under both conditions. The maximum was observed at 3.5 bar, with 2.0 L/m²·s at 900 mL/min and 2.3 L/m²·s at 1100 mL/min, representing an increase of nearly 200% compared to the initial pressure. Although the effect of flow rate was less pronounced than that of pressure, consistent differences were observed in favor of 1100 mL/min, particularly at higher pressures, where flux was approximately 0.3 L/m²·s higher than at 900 mL/min. Overall, these findings suggest that TMP determines the magnitude of flux, while higher flow rates provide a complementary benefit under high-pressure conditions by improving transport efficiency and mitigating resistance associated with concentration polarization.

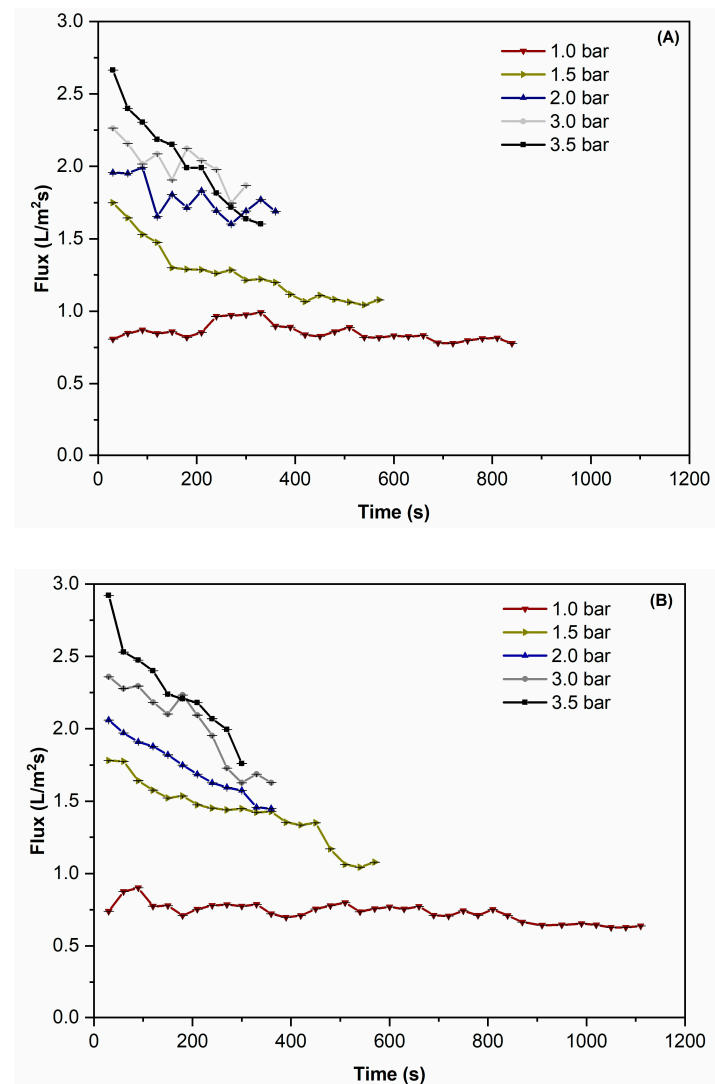


Figure 2. Effect of different transmembrane pressures on flux over time at a copper concentration of 1800 ppm for two flow rates: 900 mL/min (A) and 1100 mL/min (B).

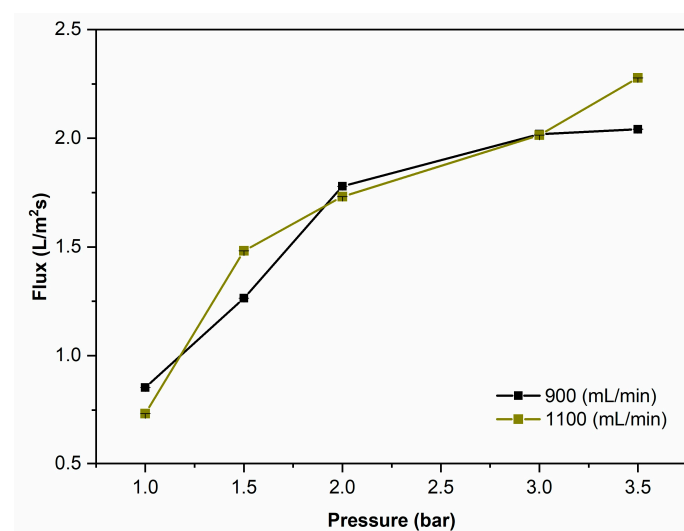


Figure 3. Effect of pressure on flux at flow rates of 900 and 1100 mL/min.

On the other hand, Figure 3 also shows that the limiting flux value reached at 900 mL/min was 2.02 L/m²·s, with a corresponding critical TMP of 2.0 bar. Similarly,

for 1100 mL/min, the limiting flux was $2.01 \text{ L/m}^2\cdot\text{s}$ and the critical TMP was also 2.0 bar. Based on these results, and to prevent the development of detrimental fouling, a feed pressure of 1.0 bar was selected for subsequent analyses. This value, being below the critical TMP of 2.0 bar, ensures operation in the subcritical region, thereby reducing the likelihood of irreversible fouling formation.

3.3. Assessment of Membrane Fouling Mechanisms

The results obtained from Hermia's fouling models modified by Field and co-workers (Figure 4A–D) show that the filtration behavior cannot be explained by a single fouling mechanism. The analysis was carried out at a transmembrane pressure of 1.0 bar, previously identified as the most stable and representative operating point for system evaluation. In the case of complete blocking (Figure 4A), the values obtained fell within the negative range, indicating that this model does not adequately describe the observed behavior, since the experimental tests did not exhibit the immediate and total pore obstruction assumed by this mechanism. The standard blocking model (Figure 4B) aligned reasonably well with the experimental data, showing well-defined linear relationships for both flow rates (900 and 1100 mL/min). In turn, the intermediate blocking model (Figure 4C) displayed a slight upward trend over time for both flow rates, suggesting that some pores were progressively affected without leading to full occlusion. Finally, the cake filtration model (Figure 4D) fitted well to the experimental data, showing a sustained increase of $1/J_p$ over time, particularly at 1100 mL/min, where the regression slope was more pronounced. Overall, these results indicate that fouling corresponds to a combination of mechanisms, in which surface deposition and partial pore blocking can coexist depending on the operating conditions. Furthermore, the statistical analysis of model fitting confirmed the complex and multifactorial nature of membrane fouling.

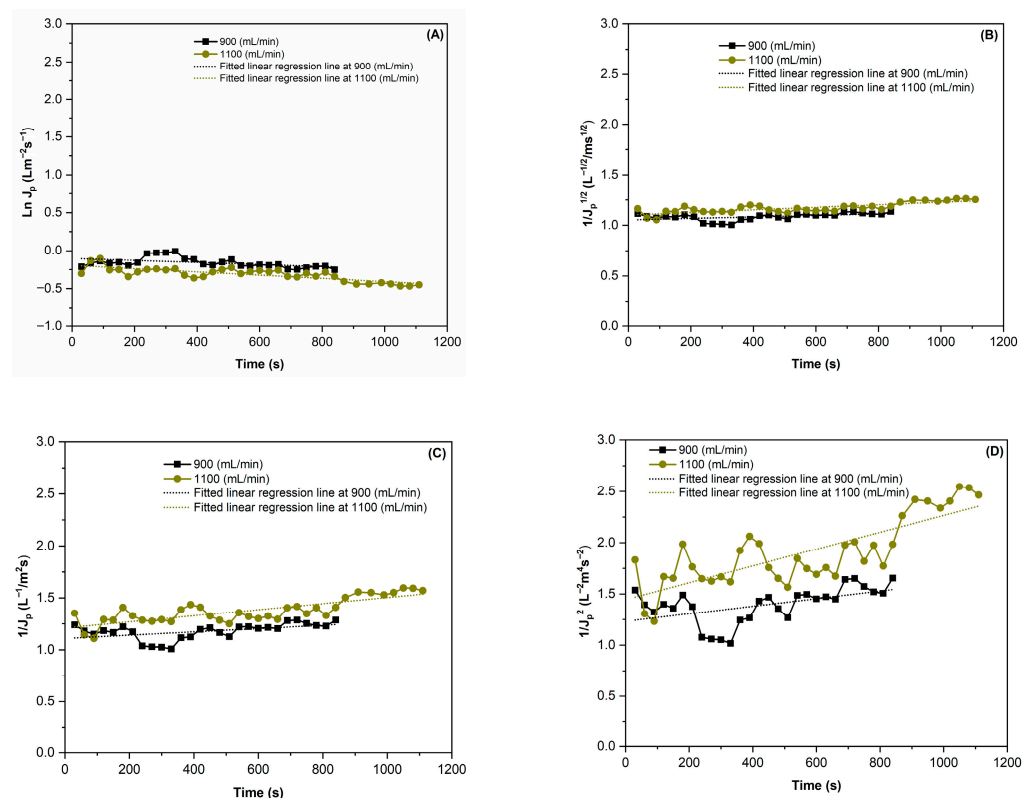


Figure 4. Permeate flow predicted by Hermia's models modified by Field and co-workers for different fouling mechanisms: complete blocking (A), standard blocking (B), intermediate blocking (C), and cake filtration (D), including fitted regression lines for flow rates of 900 and 1100 mL/min.

The statistical evaluation of the fitted Hermia fouling models modified by Field and co-workers allowed assessing both fitting and predictive performance. Table 1 summarizes the estimated fouling constants for each mechanism, together with the corresponding R^2 , RMSPE, and p -values from the S-W and K-S tests. Experiments were performed at multiple transmembrane pressures; however, only the results for 1.0 bar are reported, as this condition produced more stable flux profiles. For a given flow rate, R^2 values were comparable among the four fouling models, averaging approximately 0.25 for 900 mL/min and 0.63 for 1100 mL/min. This indicates that, under identical flow conditions, all mechanisms explained a similar proportion of the data variance, with improved predictive performance at 1100 mL/min, as reflected in the higher R^2 values. A consistent trend was observed for the RMSPE, with similar values across fouling models at the same flow rate, averaging 5.71% for 900 mL/min and 5.39% for 1100 mL/min.

Table 1. Fitted parameters and statistical analysis of Hermia’s fouling models modified by Field and co-workers, for the two flow rates studied (900 and 1100 mL/min) at a TMP of 1.0 bar.

Fouling Model (Model-Specific Exponent)	Fouling Rate Constant and Statistical Performance Metrics	Flow Rate, mL/min	
		900	1100
Complete blocking ($n = 2$)	K	-1.34×10^{-4}	-2.12×10^{-4}
	R^2	0.24	0.62
	RMSPE %	5.70	5.32
	K-S test (p -value)	0.06	0.11
	S-W test (p -value)	3.20×10^{-3}	4.33×10^{-3}
Standard blocking ($n = 1.5$)	K	7.24×10^{-5}	1.25×10^{-4}
	R^2	0.24	0.62
	RMSPE %	5.70	5.36
	K-S test (p -value)	0.44	0.73
	S-W test (p -value)	0.01	0.08
Intermediate blocking ($n = 1$)	K	1.57×10^{-4}	2.94×10^{-4}
	R^2	0.25	0.63
	RMSPE %	5.71	5.39
	K-S test (p -value)	0.42	0.68
	S-W test (p -value)	0.01	0.07
Cake formation ($n = 0$)	K	3.69×10^{-4}	8.21×10^{-4}
	R^2	0.26	0.64
	RMSPE %	5.73	5.48
	K-S test (p -value)	0.59	0.64
	S-W test (p -value)	0.02	0.05

In terms of fouling constants, K values were of the same order of magnitude (10^{-4}) across mechanisms, but generally higher at 1100 mL/min, consistent with the greater transport of foulants to the membrane surface under higher shear conditions. Regarding residual normality, the K-S test yielded p -values ≥ 0.05 for most models at both flow rates, while the S-W test was more restrictive, frequently falling below the 0.05 threshold. This indicates that although at least one test criterion of normality was satisfied in all cases, deviations were more pronounced in the S-W test, highlighting the limitations of normality in residuals. Taken together, these results suggest that while none of the Hermia models modified by Field and co-workers provided a uniquely superior fit, their predictive reliability was consistently enhanced at 1100 mL/min, reinforcing that fouling in this system is multifactorial and flow dependent.

Other variables can significantly influence process performance, including membrane pore size, copper and zinc concentrations, sulfide stoichiometric dosage, and the CN/Cu molar ratio. The effects of these factors were extensively investigated in our previous studies using ceramic membranes [22,25,28,30,32,38]. Since the objective of this work was to validate the performance of polymeric membranes in terms of flux and fouling behavior, the effect of other process variables could be extrapolated from the results presented here.

However, future studies should confirm whether polymeric membranes exhibit similar responses to those observed with ceramic membranes.

3.4. Membrane Permeability and Recovery Analysis

The chemical cleaning tests summarized in Table 2 reveal marked differences in permeability recovery depending on the cleaning solution and immersion time. Application of NaCN alone resulted in relatively limited effectiveness, with recoveries ranging from 52.5% after 1 h to 62.7% after 24 h, indicating only modest improvement with prolonged immersion. In contrast, the oxidizing mixture of HCl + H₂O₂ achieved substantially higher efficiencies, with recoveries of 76.1% at 2 h and up to 96.1% after 24 h, clearly demonstrating the positive impact of extended exposure. The combined treatment with HCl + H₂O₂ + NaCN was the most effective strategy, yielding recoveries of 85.4% (1 h) and 89.7% (2 h), and reaching 103.0% after 24 h, at which point the post-test permeability ($1.55 \times 10^{-8} \text{ m}^3/\text{m}^2 \cdot \text{s}$) slightly exceeded the initial value. This higher permeability value could suggest partial structural damage to the polymeric membrane following prolonged chemical exposure. Although the membrane permeability results suggest possible structural damage when using the third cleaning solution, the use of the other two solutions does not necessarily indicate that damage occurred. Comprehensive membrane characterization after the cleaning stage is required to confirm the type of damage and to identify the specific solution responsible. Therefore, further studies should focus on the chemical resistance of polymeric membranes during the cleaning stage. In addition, future studies should include a complete membrane characterization (SEM-EDX, FTIR, AFM) before and after the cleaning process to confirm potential damage and identify the type of structural changes that may occur during chemical cleaning. Overall, these results strongly support the existence of a synergistic effect between oxidizing agents and NaCN, enabling more efficient foulant removal and leading to near-complete recovery of membrane permeability, in some cases even enhanced.

Table 2. Evaluation of membrane recovery under different cleaning conditions.

Immersion Time, h	Cleaning Solution	Initial Permeability, $\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$	Post-Test Permeability, $\text{m}^3/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$	% Recovery
1	NaCN	1.57×10^{-8}	8.22×10^{-9}	52.5
2	NaCN	1.58×10^{-8}	9.52×10^{-9}	60.4
24	NaCN	1.61×10^{-8}	1.01×10^{-8}	62.7
1	HCl + H ₂ O ₂	1.62×10^{-8}	1.27×10^{-8}	78.5
2	HCl + H ₂ O ₂	1.33×10^{-8}	1.01×10^{-8}	76.1
24	HCl + H ₂ O ₂	1.41×10^{-8}	1.35×10^{-8}	96.1
1	HCl + H ₂ O ₂ + NaCN	1.26×10^{-8}	1.08×10^{-8}	85.4
2	HCl + H ₂ O ₂ + NaCN	1.60×10^{-8}	1.43×10^{-8}	89.7
24	HCl + H ₂ O ₂ + NaCN	1.50×10^{-8}	1.55×10^{-8}	103.0

It is relevant to consider that the use of cyanide, hydrogen peroxide, and hydrochloric acid requires the implementation of appropriate safety design criteria and operational protocols to ensure operator safety. In addition, the material specifications of the equipment must take into account the compatibility with this chemical mixture.

3.5. Capital and Operational Cost Comparison of Polymeric and Ceramic Membranes

A comparative assessment of CAPEX and OPEX costs for polymeric and ceramic membranes under simulated industrial-scale conditions is presented in Table 3. The case study was based on a feed flow rate of 200 m³/h, with a copper concentration of 1800 mg/L

(corresponding to a WAD cyanide concentration of 2500 mg/L). The results show that both membrane types exhibit similar investment requirements, with values of 46.1 US\$/m³/h for ceramic and 41.5 US\$/m³/h for polymeric membranes. This difference of lower than 10.0% indicates that polymeric membranes offer a slightly lower capital cost per installed capacity. A comparable trend was observed for the operational costs, where ceramics reached 8.6 US\$/m³ and polymeric membranes 8.4 US\$/m³, representing a difference of ~2.3%. These differences arise from the variation in unit costs between ceramic (400 US\$/m²) and polymeric membranes (60 US\$/m²). On the one hand, this directly influences the acquisition cost in the CAPEX calculation and the membrane replacement cost in the OPEX. On the other hand, the overall differences in both cases remain smaller than the unit cost difference because membrane acquisition represents only ~1% of the total CAPEX, while membrane replacement accounts for about 0.2% of the total OPEX [30]. These results suggest that, from an economic perspective, polymeric membranes are marginally more cost-efficient in both CAPEX and OPEX, although the differences are minimal. Thus, this analysis must be complemented with technical aspects such as the service life of each membrane type, their resistance to extreme conditions (e.g., pH, temperature, oxidants), ease of cleaning, and replacement frequency, considering the overall impact of membrane costs in the process. Studies such as Estay et al. (2021) [30] and Dashtban Kenari et al. (2025) [3] have demonstrated that, despite their higher cost, ceramic membranes can withstand more aggressive conditions, reduce replacement frequency, and maintain stable operation over more extended periods, which could result in lower cumulative costs. Consequently, the selection of the most suitable technology should not rely solely on a unit CAPEX/OPEX comparison, but rather on a comprehensive evaluation that simultaneously considers technical, economic, and long-term sustainability criteria, ensuring process continuity and overall competitiveness.

Table 3. Comparative CAPEX and OPEX assessment of polymeric and ceramic membranes.

Type of Membrane	CAPEX Per Capacity, US\$/m ³ /h	OPEX Per Capacity, US\$/m ³	Reference
Ceramic	46.1	8.6	[30]
Polymeric	41.5	8.4	---

4. Discussion

The permeate flux behavior observed for both operating flow rates (900 and 1100 mL/min) can be primarily attributed to the progressive fouling of the membrane, caused by the accumulation of inorganic compounds such as copper sulfide on the membrane surface and/or within the pores. This trend is consistent with previous reports on membrane systems in the presence of metal complexes [21,32]. Although higher pressures (3.0–3.5 bar) promoted higher initial fluxes, they also accelerated permeability loss, likely due to fouling layer compression and intensified concentration polarization phenomena [39]. Conversely, with lower pressures (1.0–1.5 bar), fluxes were more stable over time, albeit at lower absolute values.

Barros et al. (2025) [32] demonstrated that copper concentrations near 1800 mg/L favor the formation of compact cakes layers on membrane surfaces, which markedly reduce permeability, especially under high-pressure conditions.

On the other hand, Menzel et al. (2021) [21] reported that efficient copper recovery from AMD can be achieved with membranes, provided that hydrodynamic conditions are adequately controlled. Taken together, these findings underscore the importance of optimizing operating pressure by considering both the chemical composition of the feed and the physicochemical properties of the polymeric material. In practical terms, moderate

pressures around 1 bar appear to represent the most suitable balance between productivity and fouling control for the treatment of mining effluents.

The statistical analysis of fouling mechanisms conducted in this study revealed the absence of a single dominant mechanism, in agreement with the findings of Barros et al. (2025) [32]. Nevertheless, SEM-EDX characterization in that study suggested that cake formation was the predominant fouling mechanism, although the evidence also pointed to a combined contribution of multiple fouling processes.

Regarding membrane recovery after cleaning processes, previous studies [32] reported that effective cleaning solutions applied to ceramic membranes achieved recovery rates ranging from 52.5% to 103%. Menon et al. (2021) [44], based on FTIR analysis, demonstrated that exposure of PVDF membranes to 0.6 M HCl for 24 h induced the formation of carbon-carbon double bonds, a clear indication of dehydrofluorination. SEM images further revealed that HCl-treated membranes exhibited enlarged perforations within the membrane structure. Consequently, the authors concluded that repeated cleaning cycles with such chemicals could result in premature membrane aging in less than seven months of operation. On the other hand, Li et al. (2019) [45] showed that H₂O₂ had no appreciable effect on the PES membrane surface. The use of cyanide as a cleaning reagent must comply with rigorous safety protocols to ensure operator protection. In this context, applying membrane clarification for metal sulfide precipitates in cyanide-containing solutions is consistent with the safety standards already implemented in gold cyanidation plants. However, the use of this technology in other industrial sectors will require the evaluation of alternative cleaning agents, such as glycine [21].

From an economic standpoint, the comparison between polymeric and ceramic membranes revealed only marginal differences, as other cost components become more decisive at the full-plant scale. This was also observed in the studies by Jarvis et al. (2022) [46]; Park (2015) [47]; and Jarrar et al. (2024) [48], which showed that, despite the higher initial CAPEX of ceramic membranes, the unit cost per m³ tends to converge between materials. These studies report values of ~US\$0.27–0.28/m³ in MF/UF plants with marginal gaps between ceramic and polymeric membranes. Nevertheless, the application of polymeric membranes for clarifying metal sulfide precipitates requires further studies, specifically addressing the long-term chemical stability of the membrane material under repeated chemical cleaning protocols. Despite this limitation, the present study provides evidence supporting the technical and economic feasibility of employing polymeric membranes as an alternative to ceramic ones for this type of application. Jarvis et al. (2022) [46] compared ceramic and polymeric membranes for potable water treatment and reported that, although ceramic membranes entail higher CAPEX due to the cost of the membrane material, they result in lower OPEX when membrane replacement and labor costs are considered. Consequently, procurement approaches that offset CAPEX or rely on accurate OPEX forecasting may favor ceramic over polymeric membrane systems.

5. Conclusions

This study demonstrated the technical feasibility of integrating copper sulfide precipitation with polymeric PVDF microfiltration membranes as an effective alternative for clarifying metallurgical effluents. The results confirmed that membrane performance is highly sensitive to operating conditions, with moderate transmembrane pressures (<2 bar) and elevated flow rates (~1100 mL/min) providing the most favorable balance between permeate productivity and fouling control. Fouling was identified as a multifactorial process involving both pore blocking and cake formation, underscoring the importance of optimized hydrodynamic conditions. Chemical cleaning protocols were found to be critical for ensuring process sustainability. Oxidizing solutions (HCl + H₂O₂) and combined

treatments with NaCN achieved complete permeability recovery; however, the potential for polymer degradation under prolonged exposure suggests the need for careful assessment of membrane aging.

From a techno-economic perspective, polymeric membranes exhibited only marginal differences compared to ceramic membranes, achieving slight reductions in CAPEX (10%) and OPEX (2.3%) while maintaining comparable separation efficiency. Overall, the findings position polymeric membranes as a technically viable and economically competitive alternative for copper sulfide clarification. Nonetheless, long-term durability under repeated chemical cleaning cycles remains a key challenge. Future research should address membrane material modifications, durability enhancement strategies, and full life-cycle assessments to ensure reliable industrial-scale implementation in line with circular economy principles and sustainable mining practices.

Author Contributions: Conceptualization, H.E. and R.R.-F.; methodology, N.B. and L.B.; validation, H.E. and R.R.-F.; formal analysis, H.E., M.Q., E.T. and K.P.; investigation, M.Q. and N.B.; resources, H.E.; data curation, N.B., M.Q., K.P. and E.T.; writing—original draft preparation, M.Q., N.B. and E.T.; writing—review and editing, H.E., R.R.-F. and E.T.; visualization, M.Q., H.E. and E.T.; supervision, E.T. and H.E.; project administration, H.E.; funding acquisition, H.E. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Agency of Research and Development (ANID Chile) through the ANID projects AFB 230001 and FONDEF ID1720021.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AMD	Acid mine drainage
CA	Cellulose acetate
CAPEX	Capital expenditures
CTMP	Critical transmembrane pressure
FSF	Polysulfone
K-S	Kolmogorov–Smirnov
MF	Microfiltration
OPEX	Operational expenditures
PVDF	Polyvinylidene fluoride
R ²	Coefficient of determination
RMSPE	Root mean square percentage error
SART	Sulphidization, acidification, recycling, and thickening
SDG	Sustainable development goal
S-W	Shapiro–Wilk
TMP	Transmembrane pressure
UF	Ultrafiltration

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